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1	Your reference	SYN 60004
2	Patent application number *(The Patent Office will fill in this part)*	04 DEC 2002 0228268.9
3	Full name, address and postcode of the or of each applicant (underline all surnames)	JOHNSON MATTHEY PLC 2-4 Cockspur Street Trafalgar Square London SW1Y 5BQ
	Patents ADP Number *(if you know it)*	
	If the applicant is a corporate body, give the country/state of its incorporation	United Kingdom 851980300l
4	Title of the invention	Catalyst and process
5	Name of Your Agent *(if you have one)*	GIBSON, Sara Hillary Margaret
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	Synetix Intellectual Property Department PO Box 1, Room N205 Belasis Avenue Billingham Cleveland England, TS23 1LB
	Patents ADP Number *(if you know it)*	7912474003
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CATALYST AND PROCESS

The invention concerns a novel organometallic catalyst which is particularly suitable for use in the manufacture of polyurethane materials and also processes for the manufacture of polyurethanes using the organometallic catalysts.

Catalysts comprising compounds of titanium or zirconium are well known for use in many applications such as in esterification reactions and for curing reaction mixtures containing isocyanate and hydroxylic species to form polyurethanes. Typically, such catalysts comprise a metal alkoxide, such as titanium tetra isopropoxide, or a chelated species derived from the alkoxides.

In polyurethane manufacture the catalysts of choice in many applications have, for many years, been organic mercury and tin compounds. This is because these catalysts provide a desirable reaction profile which offers an initial induction period in which the reaction is either very slow or does not take place, followed by a rapid reaction which continues for sufficient time to produce a relatively hard polymer article. The induction time, also known as the "cream time", is desirable because it allows the liquid reaction mixture to be poured or moulded after addition of the catalyst and therefore gives the manufacturer more control over the manufacturing process. The rapid and complete reaction after the cream time is important to provide finished articles which are not sticky and which develop their desired physical properties quickly to allow fast turnaround in the production facility.

It is, however, known that mercury compounds are toxic and so there is a need for catalysts which do not contain mercury and yet which offer the manufacturer the desirable reaction profile which is offered by the known mercury-containing catalysts. Tin catalysts, such as dibutyltin dilaurate, are used extensively in polyurethane manufacture and are especially widely used in the manufacture of polyurethane foam articles. However, there are some concerns about the use of tin catalysts, especially in applications where people are exposed to the finished article for long periods, e.g. in furniture foam or shoe soles, because they may contain undesirable alkyl tin impurities. Although titanium alkoxides provide very effective catalysts for polyurethane cure reactions, they do not produce a reaction profile with the desirable cream time and cure profile described above. In many cases the reaction may be very rapid but offers no induction period and so the polyurethane mixture tends to gel very quickly, often before it can be cast into its final shape. A further problem is that, despite the rapid initial reaction, the resulting polyurethane does not achieve a satisfactory degree of cure within a reasonable time. This results in finished articles which are sticky and difficult to handle and which may have inferior physical properties compared with articles made using a mercury catalyst.

It is an object of the invention to provide a catalyst compound which does not contain mercury or tin

compounds and which may be used to manufacture polyurethane articles. It is a further object of the invention to provide a catalyst which is stable in contact with water so that it may be used in polyurethane compositions and reactant formulations intended for polyurethane foams which often contain water as a blowing agent.

Monoalkoxytitanates such as titanium monoisopropoxy tris(isostearate) are well known for use as coupling agents between inorganic materials and organic polymeric materials. For example US-A-4397983 discloses the use of isopropyl tri(dodecylbenzenesulfononyl) titanate and isopropyl tri(dioctylphosphato) titanate for coupling fillers in polyurethanes.

US-A-4122062 describes organotitanates having one of the following formulas:

a) $(RO)_z Ti(A)_x (B)_y$ or

b) $(RO)Ti(OCOR')_p(OAr)_q$ wherein R is a monovalent alkyl, alkenyl, alkynyl, or aralkyl group having from 1 to 30 carbon atoms or substituted derivatives thereof; A is a thioaroxy, sulfonyl, sulfinyl, diester pyrophosphate, diester phosphate, or a substituted derivative thereof; OAr is aroxy; B is OCOR' or OAr; R' is hydrogen or a monovalent organic group having from 1 to 100 carbon atoms; x+y+z equal 4; p+q equal 3; x, z and q may be 1, 2 or 3; and y and p may be 0, 1 or 2; the reaction products of such organo-titanates and comminuted inorganic material; and polymeric materials containing such reaction products

US-A-4094853 describes a composition of matter comprising the reaction product of a comminuted inorganic material and an organo-titanate having the formula $(RO)Ti(OCOR')_3$ wherein R is a monovalent alkyl, alkenyl, alkynyl or aralkyl group having from 1 to 30 carbon atoms or a substituted derivative thereof, R' is a monovalent organic group the total number of carbon atoms in the three R' groups in a molecule being not more than 14; and polymeric materials containing such reaction products.

EP-A-0164227 describes neoalkoxy compounds having the formula $R R^1R^2 CCH_2OM(A)_a(B)_b(C)_c$ wherein M is titanium or zirconium, R, R^1 and R^2 are each a monovalent alkyl, alkenyl, alkynyl, aralkyl, aryl or alkaryl group having up to twenty carbon atoms or a halogen or ether substituted derivative thereof, and, in addition, R^2 may also be an oxy derivative or an ether substituted oxy derivative of said groups; A, B, and C are each a monovalent aroxy, thioaroxy, diester phosphate, diester pyrophosphate, oxyalkylamino, sulfonyl or carboxyl containing up to 30 carbon atoms; and a + b + c = 3. The compound is useful as a coupling and polymer processing agent and compositions containing the compound and methods of preparing polymeric material including the compound are also described.

GB-A-1509283 describes novel organo-titanates represented by the formula:

$Ti(OR)_{4-n}(OCOR')_n$ where OR is a hydrolyzable group; R' is a non-hydrolyzable group; and n is between about 3.0 and 3.50, preferably from 3.1 to 3.25. R, may be a straight chain, branched or cyclic alkyl group having from 1 to 5 carbon atoms per molecule. The non-hydrolyzable groups (OCOR') are preferably formed from organic acids having 6 to 24 carbon atoms, such as stearic, isostearic, oleic, linoleic, palmitic, lauric and tall oil acids.
The compounds are used for treating inorganic solids to improve the dispersion of the inorganic solids in polymeric compounds and to improve the physical properties of the filled polymeric compounds, i.e. the organo-titanates are used as coupling agents.

Monte and Sugerman (Journal of Cellular Plastics, November-December 1985, p385) describe the use of various neoalkoxytitanates and neoalkoxyzirconates as coupling agents in different polymer systems. They conclude that certain of the compounds are capable of directly catalysing the polyol-isocyanate reaction in addition to bonding polymer to substrate.

US-A-2846408 describes a process for preparing cellular polyurethane plastics of specified pore structure using metallic compounds defined by the general formula $Me(OR)_mX_{n-m}$ where R is alkyl and X is an organic carboxylic acid radical including lauric, stearic, palmitic, naphthenic and phenylacetic acids, m is at least 1 and n is the valence of the metal Me. Me includes titanium, zirconium and tin.

US-A-2926148 describes catalysts for the reaction between a diisocyanate and a mixture of alcohols to form resins. The catalysts include, apart from tin compounds, tetralkyl titanates and zirconates and various titanium esters which include triethanolamine titanate-N-stearate, triethanolamine titanate-N-oleate, octylene glycol titanate and triethanolamine titanate.

US-A-6133404 describes the use of monoalkoxytitanates as additives useful in the preparation of biodegradeable polyester compositions.

US-A-5591800 describes the manufacture of polyesters using a cyclic titanium catalyst such as a titanate compound formed by the reaction of a tetra-alkyl titanate and a triol.

US-A-5,902,835 describes titanium, zirconium or hafnium blowing catalyst compositions for the production of polyurethane foams in which the blowing catalyst is a compound represented by the following formulae: [M(L1)(L2)(L3)(L4)]n, [M(L1)(L2)(L3)]n, [M(L1)(L2)]n, [M(L1)]n wherein M is titanium, zirconium, or hafnium; n ranges from 1 to 20; and each of L1, L2, L3, and L4 is the same or different ligand selected from the following groups: (1) oxygen, sulphur and nitrogen; (2) an alcoholate, phenolate, glycolate, thiolate, carboxylate, dithiocarbamate, aminate, aminoalcoholate, phosphate, phosphonate, pyrophosphate, sulfonate, or silylamide any of which contains from 1 to 20

carbon atoms and, optionally, contains one or more functional groups, or oxygen, sulphur, nitrogen, or phosphorus-containing; (3) a chelating ligand, such as, various non-fluorine containing and non-sterically hindered beta -diketones, triethanolamine, salicylaldehyde, and salicylamide.

In GB-A-2314081, an esterification catalyst comprising the reaction product of an alkoxide or condensed alkoxide of titanium or zirconium, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base. In that patent, the preferred amount of base for monobasic 2-hydroxy acids such as lactic acid, is in the range 0.8 to 1.2 mole per mole of 2-hydroxy acid. In the case of citric acid (a tribasic acid), the preferred amount is in the range 1 to 3 moles base per mole of 2-hydroxy acid. We have found that when a catalyst composition of the type described in GB-A-2314081 is made using 1,4-butane diol as the dihydric alcohol and an inorganic base is present in the preferred concentration range, the 1,4-butane diol forms a complex with the base leading to formation of a gelled product which is not suitable for use as a catalyst.

According to the invention we therefore provide a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base, wherein the molar ratio of base to 2-hydroxy carboxylic acid is in the range 0.01 – 0.79:1.

According to a further aspect of the invention, we also provide a composition comprising:

a) either
   i) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or
   ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

b) a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base, wherein the molar ratio of base to 2-hydroxy carboxylic acid is in the range 0.01 – 0.79:1; and optionally

c) one or more further components selected from chain modifiers, diluents, flame retardants, blowing agents, release agents, water, coupling agents, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, colourants, impact modifiers, surfactants, thixotropic agents, flame retardants, plasticisers, and other binders.

According to a further aspect of the invention, we also provide a process for the manufacture of a polyurethane article, comprising the steps of :

a) forming a mixture by mixing together either
   i) a compound having more than one hydroxy group which is capable of reacting with an

isocyanate group -containing material to form a polyurethane or

ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

with a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide; an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base, wherein the molar ratio of base to 2-hydroxy carboxylic acid is in the range 0.01 – 0.79:1;

b) adding to said mixture the other of the compound in a)i) or a) ii) which is not already present in the mixture,
c) forming said mixture into the required shape for the polyurethane article,
d) allowing said mixture to cure
e) optionally subjecting the mixture to specified conditions for post-cure conditioning.

The compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or the compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane may comprise a mixture of such compounds or a mixture of such compounds with different compounds, e.g. fillers or other additives etc. In particular, where the polyurethane article is intended to form a foam, the mixture of polyol or isocyanate may or of the two together may contain a blowing agent or a blowing catalyst to catalyse the reaction between isocyanate and water which generates carbon dioxide to form the foam. Suitable blowing catalysts include amines, in particular tertiary amines.

The catalyst of the invention is the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base. Preferably, the alkoxide has the formula $M(OR)_x$ in which M is titanium, zirconium, hafnium, aluminium, iron (III) or a lanthanide, R is an alkyl group and x is the valency of the metal M. More preferably R contains 1 to 6 carbon atoms and particularly suitable alkoxides include tetraisopropoxy titanium, tetra-n-butoxy titanium, tetra-n-propoxy zirconium and tetra-n-butoxy zirconium, aluminium tri-*sec*-butoxide.

The condensed alkoxides suitable for preparing the catalysts useful in this invention are typically prepared by careful hydrolysis of titanium or zirconium alkoxides and are frequently represented by the formula $R^1O[M(OR^1)_2O]_nR^1$ in which R^1 represents an alkyl group and M represents titanium or zirconium. Preferably, n is less than 20 and more preferably is less than 10. Preferably R^1 contains 1 to 6 carbon atoms and useful condensed alkoxides include the compounds known as polybutyl titanate, polyisopropyl titanate and polybutyl zirconate.

Preferably the alcohol containing at least two hydroxyl groups is a dihydric alcohol e.g.1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butane diol or a dihydric alcohol containing a longer chain such as diethylene glycol or a polyethylene glycol. 1,4-butane diol is frequently used as a chain-extender in polyurethane formulations and therefore it is a preferred alcohol. The catalyst can also be prepared from a polyhydric alcohol such as glycerol, trimethylolpropane or pentaerythritol.

Preferably the catalyst is prepared by reacting a dihydric alcohol with an alkoxide or condensed alkoxide in a ratio of from 2 to 12 moles of dihydric alcohol to each mole of the titanium or zirconium. More preferably the reaction product contains 4 to 8 moles dihydric alcohol per mole of titanium or zirconium.

Preferred 2-hydroxy carboxylic acids include lactic acid, citric acid, malic acid and tartaric acid. Some suitable acids are supplied as hydrates or as aqueous mixtures. Acids in this form as well as anhydrous acids are suitable for preparing the catalysts used in this invention. The preferred molar ratio of acid to titanium or zirconium in the reaction product is 1 to 4 moles per mole of titanium or zirconium. More preferably the catalyst contains 1.5 to 3.5 moles of 2-hydroxy acid per mole of titanium or zirconium.

The base used in preparing the catalyst composition is generally an inorganic base and suitable bases include aqueous solutions of salts of weak acids with metals selected from Group IA, IIA or the periodic table of elements or with zinc, aluminium, iron(II), copper(II), nickel, cobalt (II), manganese (II), lanthanum, cerium, neodymium, and samarium. Preferred bases include sodium hydroxide, potassium hydroxide, ammonium hydroxide, lithium hydroxide, sodium carbonate, magnesium hydroxide, calcium hydroxide, aluminium acetate, zinc oxide, caesium carbonate and ammonia. The molar ratio of base to 2-hydroxy carboxylic acid is in the range 0.05 to 0.79 : 1. In the case of citric acid (a tribasic acid), the preferred amount is in the range 0.01 to 0.6 moles base per mole of 2-hydroxy acid. In general, the amount of base present is usually in the range 0.05 to 2.4 moles per mole of titanium or zirconium and preferably the amount of base is from 0.5 to 2 , especially 0.7 to 1.5 moles per mole of titanium or zirconium

It is frequently convenient to add water together with the base when preparing the catalysts.

The catalyst can be prepared by mixing the components (alkoxide or condensed alkoxide, dihydric alcohol, 2-hydroxy acid and base) with removal of any by-product, (e.g. isopropyl alcohol when the alkoxide is tetraisopropoxytitanium), at any appropriate stage. In one preferred method the alkoxide or condensed alkoxide and dihydric alcohol are mixed and subsequently, 2-hydroxy acid and then base are added or a pre-neutralised 2-hydroxy acid solution, is added. In an alternative preferred method the alkoxide or condensed alkoxide is reacted with the 2-hydroxy acid and by-product alcohol is removed. Base is then added to this reaction product followed by a dihydric alcohol to produce

the reaction product which is a catalyst in the process of the invention. If desired, further by-product alcohol can then be removed by distillation. The catalyst may be diluted in a solvent, which is may be an alcohol, for example a compound which is to be used in the polyurethane reaction. As an example the solvent may be a diol such as 1,4-butanediol which is often used as a chain extender in commercial polyol compositions supplied for polyurethane manufacture.

The compound of the invention is particularly useful as a cure catalyst for the reaction between a hydroxy-functionalised molecule, such as a polyol, and an isocyanate-functionalised molecule, such as a polyisocyanate. This reaction forms the basis of many commercially available two-component polyurethane systems. The polyol component may be any suitable for the manufacture of polyurethanes and includes polyester-polyols, polyester-amide polyols, polyether-polyols, polythioetherpolyols, polycarbonate polyols, polyacetal polyols, polyolefin polyols polysiloxane polyols, dispersions or solutions of addition or condensation polymers in polyols of the types described above, often referred to as "polymer" polyols. A very wide variety of polyols has been described in the prior art and is well known to the formulator of polyurethane materials.

Typically, a mixture of polyols is used to manufacture polyurethane having particular physical properties. The polyol or polyols is selected to have a molecular weight, backbone type and hydroxy functionality which is tailored to the requirements of the formulator. Typically the polyol includes a chain extender, which is often a relatively short-chain diol such as 1,4-butane diol or diethylene glycol or a low molecular weight polyethylene glycol. Alternative chain extenders in commercial use, such as diamines, e.g. MOCA (4,4-methylene bis (2-chloroaniline)) may also be used.

The isocyanate compositions used for polyurethane manufacture suitable for use with the catalysts of the present invention may be any organic polyisocyanate compound or mixture of organic polyisocyanate compounds which are commercially useful for the purpose. Suitable organic polyisocyanates include diisocyanates, particularly aromatic diisocyanates, and isocyanates of higher functionality. Examples of suitable organic polyisocyanates include aliphatic isocyanates such as hexamethylene diisocyanate and isophorone diisocyanate; and aromatic isocyanates such as m- and p-phenylene diisocyanate, tolylene-2,4- and tolylene- 2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, chlorophenylene- 2,4-diisocyanate, naphthylene-1,5-diisocyanate, diphenylene-4,4'-diisocyanate, 4,4'-diisocyanate-3,3'-dimethyl-diphenyl, 3-methyldiphenylmethane-4,4'-di- isocyanate and diphenyl ether diisocyanate; and cycloaliphatic diisocyanates such as cyclohexane-2,4- and -2,3-diisocyanate, 1-methylcyclohexyl-2,4- and -2,6-diisocyanate and mixtures thereof and bis-(isocyanatocyclohexyl)methane and triisocyanates such as 2,4,6-triisocyanatotoluene and 2,4,4-tri-isocyanatodiphenylether.

Modified polyisocyanates containing isocyanurate, carbodiimide or uretonimine groups may be used. The polyisocyanate may also be an isocyanate-ended prepolymer made by reacting an excess of a diisocyanate or higher functionality polyisocyanate with a polyol for example a polyether polyol or a polyester polyol. The use of prepolymers is common in commercially available polyurethane systems. In these cases, polyols may already be incorporated in the isocyanate or prepolymer whilst further components such as chain extenders, polyols etc may be mixed with the isocyanate prepolymer mixture before polymerisation.

Mixtures of isocyanates may be used in conjunction with the organometallic composition of the invention, for example a mixture of tolylene diisocyanate isomers such as the commercially available mixtures of 2,4- and 2,6-isomers. A mixture of di- and higher polyisocyanates, such as trimers (isocyanurates) or pre-polymers, may also be used. Polyisocyanate mixtures may optionally contain monofunctional isocyanates such as p-ethyl phenylisocyanate.

Preferably the polyisocyanate is liquid at room temperature.

The organometallic composition of the invention is typically added to the polyol prior to mixing together the polyol component with the isocyanate component to form the polyurethane. However, the organometallic composition may instead be added to the isocyanate component if required.

A composition containing a catalyst composition of the present invention and a polyisocyanate and compounds reactive therewith may further comprise conventional additives such as chain modifiers, diluents, flame retardants, blowing agents, release agents, water, coupling agents, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, colourants, impact modifiers, surfactants, thixotropic agents, flame retardants, plasticisers, and other binders. The selection of these and other ingredients for inclusion in a formulation for a polyurethane composition is well known to the skilled person and may be selected for the particular purpose.

When the mixture has been allowed to cure it may be further conditioned to allow for post-cure. Typically this occurs when the polyurethane article, coating etc has hardened to a state in which it may be handled, de-moulded etc and then it may be held at elevated temperature, e.g. by placing in an oven, to develop or enhance the full cured properties of the article.

The catalysts of the present invention are useful for the manufacture of polyurethane foams, flexible or rigid articles, coatings, adhesives, elastomers, sealants, thermoplastic polyurethanes, and binders e.g. for oriented strand board manufacture. The catalysts of the present invention may also be useful in preparing polyurethane prepolymers, i.e. urethane polymers of relatively low molecular weight which are supplied to end-users for curing into polyurethane articles or compositions of higher

molecular weight.

The catalysts are typically present in the isocyanate and/or alcohol mixture to give a concentration in the range 1 x 10^{-4} to 10% by weight, preferably up to about 4% by weight based upon the weight of the total reaction system, i.e. the total weight of the polyisocyanate and polyol components .

The invention is illustrated by the following examples.

EXAMPLE 1

Water (52.25g, 2.90 moles) and citric acid monohydrate (75g, 0.36 moles) were placed into a pre-weighed rotary evaporator flask, and heated for 15 minutes to dissolve the citric acid. The solution was allowed to cool. A vacuum was applied to the flask and titanium (IV) n-butoxide (48.5g, 0.14 moles) (VERTEC™ TNBT) added via vacuum inlet. An azeotrope of n-butanol/water was removed under reduced pressure. The resulting mixture was allowed to cool before the dropwise addition of 5% magnesium hydroxide in water (145g, 0.125 moles). 1,4-butanediol (103 g, 1.14 moles) was then added dropwise, whilst stirring. An azeotrope of n-butanol/water was removed under reduced pressure. The resulting mixture was allowed to cool before 50% dilution with 1,4-butanediol to yield a slightly hazy solution with a titanium content of 1.54%.

EXAMPLE 2

Example 1 was repeated except that 5% lithium hydroxide in water (105g, 0.125 moles) was added in place of the magnesium hydroxide. The resulting mixture was allowed to cool before 50% dilution with 1,4-butanediol to yield a slightly hazy solution with a titanium content of 1.33%.

EXAMPLE 3

Example 1 was repeated except that 5% aluminium acetate ($(CH_3CO_2)_2AlOH$) in water (408g, 0.125 moles) was added in place of the magnesium hydroxide. The resulting mixture was allowed to cool before 50% dilution with 1,4-butanediol to yield a slightly hazy solution with a titanium content of 1.84%.

EXAMPLE 4

Example 1 was repeated except that 5% zinc oxide in water (203, 0.125 moles) was added in place of the magnesium hydroxide. The resulting mixture was allowed to cool before 50% dilution with 1,4-butanediol to yield a slightly hazy solution with a titanium content of 2.10%.

EXAMPLE 5

Example 1 was repeated except that 5% caesium carbonate in water (407g, 0.125 moles) was added in place of the magnesium hydroxide. The resulting mixture was allowed to cool before 50% dilution

with 1,4-butanediol to yield a slightly hazy solution with a titanium content of 1.71%.

EXAMPLE 6

50% Citric acid solution (0.18mole, 69.12g) was taken in a rotary evaporator flask to which aluminium tri-*sec*-butoxide (0.0639mole, 15.75g) was added dropwise from a dropping funnel. On stirring it dissolved giving a cloudy suspension (slightly exothermic). The mixture was distilled under vacuum at 80°C for nearly 2 hours to remove water and butanol. 50g (0.0625 mole) of a 5% (by wt) aqueous NaOH solution was added dropwise followed by 1,4 butanediol (0.57mole, 51.375g). The remaining butanol and water were removed at 110°C under vacuum.

EXAMPLE 7

Example 6 was repeated with the exception that 101.72g (0.0625 mole) of a 5% (by wt) aqueous ZnO solution was added instead of the NaOH solution.

EXAMPLE 8

The catalysts of the invention were used as catalysts in the preparation of polyurethane foams. All the catalysts were found to be hydrolytically stable and contained on average about 0.5% w/w of water.

50g of a commercial polyether polyol preparation containing an organic filler, surfactants, fillers, pigments, a tertiary amine (as blowing agent), 1,4-butane diol (chain extender) and water (for the foam blowing reaction) was placed in a disposable speed mixer cup. 0.2g of the appropriate catalyst (see Table) was added and the mixture was mixed at 3000rpm. 35g of 4,4' methylenebis phenylisocyanate (MDI) based prepolymer (%NCO = 18.4) was added and the whole mixture was hand mixed for 20 seconds, then poured into a disposable beaker. A thin wire of (HI-92704C) K-thermocouple was inserted to record the exotherm of the foaming reaction. The foam height and cream time were recorded for each mixture.

The same preparation was carried out using a commercial tin catalyst as a comparison.

The density (g/l) of the foams was measured by weighing to determine the mass and using a water displacement method to determine the volume of the foam.

The results show that foams of at least comparable density to those produced using the tin catalyst were produced using the catalysts of the invention. The longer cream times given by Examples 6 and 7 may be of benefit in some applications where time to mould the mixtures is required before the foam is formed.

In order to show the effect of the amine catalyst used, the preparations were repeated in the absence of the amine catalyst. The product polyurethane became gelled but the foams did not rise and the

exotherms were low (<40 °C) indicating that the amine catalyst used functioned as the blowing catalyst, whilst the catalysts of the invention were functioning as gelation catalysts.

Table 1

Catalyst	Foam height(mm)	Amount of catalyst (g)	Cream time (mins)	Density(g/l)	Exotherm(°C)
Example 1	50	0.2	18-21	463	91
Example 2	56	0.2	18-21	416	98
Example 3	79	0.2	18-21	311	98
Example 4	60	0.2	18-21	388	95
Example 5	49	0.2	18-21	471	94
Example 6	60	0.2	20-25	353	98
Example 6	46	0.07	20-25	447	100
Example 7	47	0.07	20-25	475	100
Example 7	45	0.06	20-25	463	98
Tin (comparison)	53	0.2	18-21	399	95

Claims

1. A catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base, wherein the molar ratio of base to 2-hydroxy carboxylic acid is in the range 0.01 – 0.79:1.

2. A catalyst composition as claimed in claim 1, wherein the alcohol is selected from the group consisting of 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butane diol, diethylene glycol and a polyethylene glycol.

3. A catalyst composition as claimed in either claim 1 or claim 2 , wherein the 2-hydroxy carboxylic acid comprises lactic acid, citric acid, malic acid or tartaric acid.

4. A catalyst composition as claimed in any of the preceding claims, wherein the molar ratio of acid to titanium or zirconium in the reaction product is from 1 to 4 moles acid per mole of titanium or zirconium.

5. A catalyst composition as claimed in any of the preceding claims, wherein the base comprises sodium hydroxide, potassium hydroxide, ammonium hydroxide, lithium hydroxide, sodium carbonate, magnesium hydroxide, calcium hydroxide, aluminium acetate, zinc oxide, caesium carbonate or ammonia.

6. A composition comprising:

a) either
   - i) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or
   - ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

b) a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base, wherein the molar ratio of base to 2-hydroxy carboxylic acid is in the range 0.01 – 0.79:1; and optionally

c) one or more further components selected from chain modifiers, diluents, flame retardants, blowing agents, release agents, water, coupling agents, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, colourants, impact modifiers, surfactants, thixotropic agents, flame retardants, plasticisers, and other binders.

7. A process for the manufacture of a polyurethane article, comprising the steps of :

a) forming a mixture by mixing together either

i) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or

ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

with a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, zirconium, hafnium, aluminium, iron (III), or a lanthanide, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base, wherein the molar ratio of base to 2-hydroxy carboxylic acid is in the range 0.01 – 0.79:1;

b) adding to said mixture the other of the compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or the a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,
c) forming said mixture into the required shape for the polyurethane article,
d) allowing said mixture to cure
e) optionally subjecting the mixture to specified conditions for post-cure conditioning.

8. A process as claimed in claim 8, wherein the polyurethane article is a foam and a blowing catalyst is added to the mixture formed in step a).

Abstract
The invention comprises a catalyst composition comprising the reaction product of an alkoxide or condensed alkoxide of titanium, aluminium or zirconium, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a base, wherein the molar ratio of base to 2-hydroxy carboxylic acid is in the range 0.01 – 0.79:1. The catalyst is useful for the production of polyurethane articles from polyisocyanate compounds and hydroxyl-containing compounds. A process for the production of polyurethanes is also included.

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